Electron-hole interaction and optical excitations in solids, surfaces, and polymers

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Abstract. The optical properties of a variety of materials have been calculated using a recently developed *ab initio* method based on solving the Bethe-Salpeter equation of the two-particle Green's functions. Relevant self-energy and electron-hole interaction effects are included from first-principles. Results on selected semiconductors, insulators, surfaces, and conjugated polymers are discussed. In many of these systems, excitonic effects are shown to dramatically alter the excitation energies and the optical spectra.

1 Introduction

It has long been recognized that electron-hole interaction effects play an important role in the optical properties of insulating materials (see e.g. [1]). In particular, these effects are crucial in the understanding of the optical response of many lower-dimensional systems since Coulomb interaction and many-electron effects are in general more dominant in these systems. In the past, it was not practical to include these effects in *ab initio* calculations. Recent theoretical advances, however, have made it now possible to include accurately electron-hole interaction in the calculation of the optical properties of a large class of materials from first principles [2-4].

The theoretical framework is based on solving a Bethe-Salpeter equation for the electron-hole amplitude of the 2-particle Green's function. The method [2] has allowed us to study the continuum absorption spectrum, as well as, the discrete bound excitonic states in a range of materials. Our approach takes into account electron self energy effects [5] and the interaction between an optically excited electron and the hole left behind [6]. We find that, in many cases, electron-hole interactions qualitatively change the behavior of the optical response. For example, the spectrum of alpha quartz [7] and those of the conjugated polymers [8] are dominated by excitonic effects up to several eV's above the absorption threshold, making them qualitatively different from the interband transition results.

2 Theory

In moderately correlated electron systems, the photo-excited states can be written, to a good approximation, as a linear combination of free electron-hole configurations,

$$|S\rangle = \sum_{cvk} A^S_{cvk} |ck;vk\rangle \tag{1}$$

where $|ck;vk\rangle$ represents a configuration in which a quasielectron is promoted from the valence band v to the conduction band c. Only vertical transitions are taken into account. From the Bethe-Salpeter equation for the two-particle Green's function, the coefficients A^S_{cvk} satisfy an eigenvalue equation [6],

$$(E_{c,k} - E_{v,k})A^S_{cvk} + \sum_{cvk,c'v'k'} \kappa^{c'v'k'}_{cvk} A^S_{c'v'k'} = \Omega^S A^S_{cvk} \tag{2}$$

where $\kappa^{c'v'k'}_{cvk}$ describes the interaction between the excited electron and hole, and Ω^S is the energy of state $|S\rangle$. In general, κ is a complex function that describes the scattering of an electron-hole pair in configuration $|ck;vk\rangle$ to $|c'k';v'k'\rangle$. Within the GW approximation for the self energy, κ can be simplified to two leading terms: a screened attractive interaction plus a bare repulsive exchange interaction. Dynamical screening can be neglected if the energies Ω^S are close to the energy of the non-interacting pairs.

The optical absorption is given by [2]

$$\varepsilon_2(\omega) = \frac{4\pi^2 e^2}{\omega^2} \frac{1}{V_c} \sum \left| \langle G | \lambda \cdot v | S \rangle \right|^2 \delta(\Omega_S - \hbar\omega) \tag{3}$$

where $|G\rangle$ is the ground state and λ and v are the polarization vector and the velocity operator, respectively. The quasiparticle energies in Eq. (2) are taken from a GW calculation, using the method of Hybertsen and Louie [5].

3 Applications

The measured absorption spectrum of silicon, plotted in Figure 1, shows two well-pronounced peaks at energies about 3.5 eV and 4.2 eV [9]. The interband transition results, which assume no electron-hole interaction, are significantly different from the measured data. The calculated results using Eq. (3) on the other hand reproduce the experiment very accurately. The minor discrepancies at the energy range 5.5-6.0 eV may be due to the finite sampling of k-points in the Brillouin zone. Compared with the non-

interacting case, the large enhancement in the amplitude of the first peak is due to excitonic effects. Also, electron-hole interaction causes a redistribution of the optical strength near 4.5 eV giving rise to a large shift in the second peak position toward lower energy, which results in a significantly better agreement with experiment.
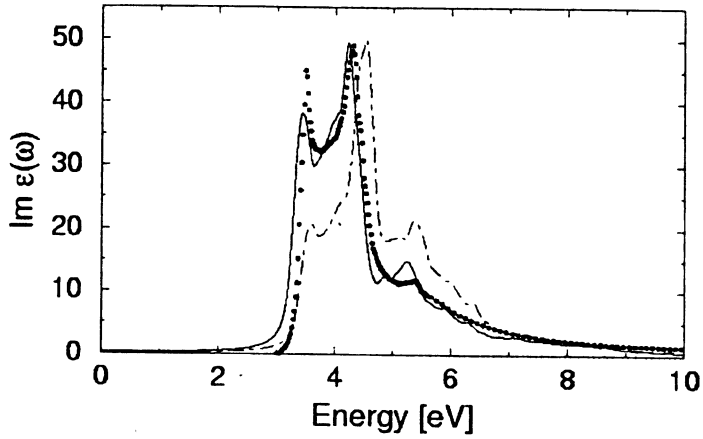
Figure 1: Absorption spectrum of bulk silicon, with (full line) and without (dotted-dashed line) excitonic effects. The experimental spectrum (dots) is from [9].
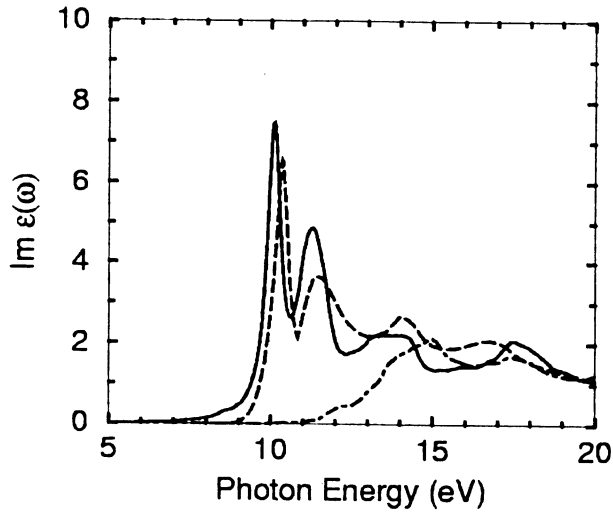
Figure 2: Absorption spectrum of alpha quartz (SiO_2) with excitonic effects (solid line) as compared to the interband transition theory (dotted-dashed line). Experimental data [10] are given by the dashed line.

As an example of a wide gap insulator, we present our results for alpha quartz in Fig. 2. The optical properties of alpha quartz (SiO_2) have been a subject of debate since the 1960's [10]. The presence of a series of four sharp peaks in its absorption spectrum has been recently shown to be due to the formation of resonant excitons [7]. In Figure 2, the optical absorption is for polarization perpendicular to the hexagonal plane. The agreement between the experimental spectrum (with peaks at energies 10.3, 11.7, 14.0 and 17.3 eV) and the calculated spectrum, with excitonic effects included, is again excellent. The fact

that an interband transition description gives an almost featureless absorption spectrum shows that the formation of optically active resonant excitonic states dominates the spectrum up to energies about 18 eV.

It is also possible to obtain the binding energy of bound excitons very accurately from Eq. (2), even when this binding energy is only a small fraction of an eV. In this case, a careful sampling of the Brillouin zone is required, so that the electronic energy bands are described with the necessary accuracy. Table 1 shows the binding energy of the lowest energy excitonic states in GaAs [2]. In this calculation, a set of over 1,000 special k-points near the position of the band extrema was used.

Table 1: Calculated binding energies of excitons in GaAs, compared with data from optical absorption [11] and from two-photon absorption[12].

	This work [meV]	Exp. [meV]
E_{1s}	4.0	4.2 [a]
E_{2s}	0.9	1.09 [a]
E_{2p}	0.2–0.7	~0.1 [b]

a) Reference [11]
b) Reference [12]
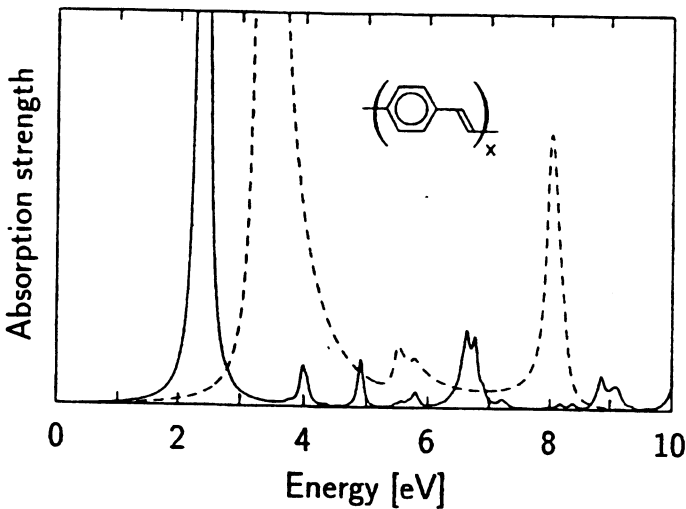
Figure 3: Calculated optical absorption spectrum of PPV, with (solid line) and without (dashed line) excitonic effects. An artificial broadening of 0.05 eV is included, and the polarization vector is along the chain.

As an example of a one-dimensional system, we present results for the conjugated polymer, poly-phenylene-vinylene (PPV), in Figure 3. The optical properties of the semiconducting polymers are far less well understood than conventional semiconductors owing to their strong electron-hole interaction. As seen in Fig. 3, the difference between the results with and without excitonic effects is striking. The peak at 2.4 eV arises from coherent coupled transitions between the highest occupied band and the lowest unoccupied band. The resulting exciton has a large binding energy of 0.9 eV. The measured absorption peaks are located at energies 2.5, 3.7, 4.8 and 6.0 eV, which are in quite good agreement with the calculated peak positions. As in the case of SiO_2, the spectrum of PPV is dominated by transitions to resonant exciton states which are greatly enhanced because of the one-dimensional nature of the system.

The reduced dimensionality at a surface can also greatly enhance excitonic effects. For example, in the case of the Si(111) 2x1 surface, we find that the surface-state optical spectrum is dominated by surface-state excitons which have binding energies that are an order of magnitude bigger than the bulk case, and one cannot interpret the experimental spectrum without considering these effects. [13] This is illustrated in Fig. 4.
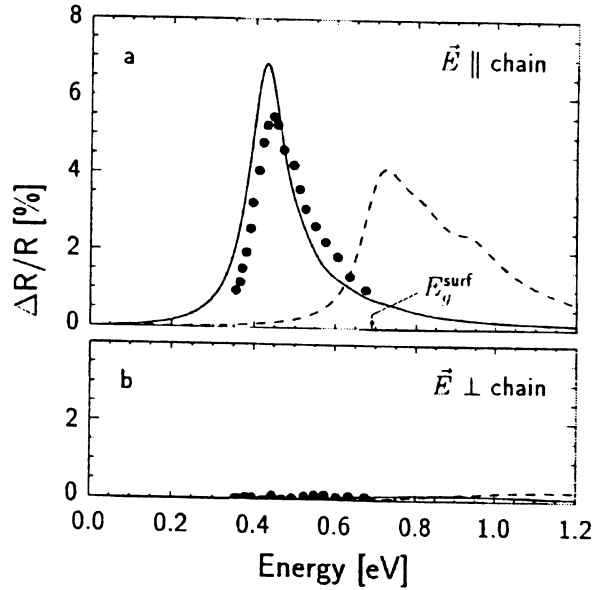
Figure 4: Calculated differential reflectivity spectrum of the Si(111)2x1 surface. Results with (without) surface-state excitonic effects are given by the solid (dashed) curve. Experimental data are given by the dots.[14]

4   Conclusion

In summary, we have shown that a recently developed *ab initio* method [2], based on solving the Bethe-Salpeter equation, is capable of describing successfully the optical properties of a variety of condensed matter systems including semiconductors, insulators, surfaces, and polymers. With electron-hole interaction included, the agreement between

the theoretical absorption spectra and experimental data is in general remarkably good. Although not discussed here, similar studies have also been performed for zero-dimensional systems including atoms and clusters [3].

Acknowledgments

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